**outline**

**Use of modern physical adsorption theories**

* **Forwards by Condon by Adolphs**
* **Purpose of this paper**
* **Definitions, Concepts and Scope:**
	+ **Adsorbate**
		- **Part of System**
	+ **Adsorbent**
		- **Part of System**
	+ **Adsorptive**
		- **The Surroundings**
	+ **Difference between Chemisorption and Physisorption**
		- **Definition of physical forces versus chemical reaction**
		- **Bases of electron topology**
* **Defined conditions considered in this report**
	+ **Temperature range**
		- **Below critical point**
		- **Above freezing point**
	+ **Adsorbent conditions**
		- **First understand homogenous, non-porous**
		- **Later add**
			* **heterogeneity**
			* **microporosity and mesoporosity**
* **A short History of traditional physical adsorption theory analysis**
	+ **Typing of isotherm for analysis**
	+ **The analogy of the BET to the Langmuir as a guide.**
	+ **The early restrictions**
	+ **Later restrictions**
		- **The restriction for a max{***n*ads(1 - *P*/*P*vap)}
	+ **The problem that the Langmuir criterion was mathematically impossible**
		- **And the impossible “B” point comparison**
		- **The “C” point problem and imaginary energy**
	+ **The IUPAC restriction on naming pore sizes.**
* **Need to abandon the BET, Langmuir isotherm and their derivatives.**
	+ **History and staying power of the BET**
		- **The development of BET and its consequences**
		- **The trials of those who were not true believers**
			* **Polanyi, DeBoer, Fuller and others.**
	+ **Definition of “Henry’s Law” isotherms.**
	+ **Achillies heel – observation of the threshold pressure**
	+ **Examples and QED**
* **Experimental precautions**
	+ **Temperature measurement and control**
		- **Baffling**
		- **Wrapping**
		- **For cryogenic**
	+ **Low pressure requirement HV or UHV – why?**
		- **Threshold measurement**
		- **Law determination**
	+ **Knudsen correction solutions:**
		- **Large tubing**
		- **Individual tubing calibration**
	+ **Outgassing of dead space or buoyancy calibration**
		- **High temperature outgassing**
		- **Calibrate after measurement**
		- **Repeating the isotherm (3 times recommended)**
* **Modern theoretical developments for replacements**
	+ **Are consistency with modern physics**
	+ **Have a simple framework of modern physics**
		- **Quantum Mechanics and Grand Canonical Partition Function**
			* **Validity for large molecules**
		- **Fluid Dynamics and Thermodynamics**
		- **Other interesting inputs from Dubinin and Fuller**
	+ **Yields results that are easy to interpret**
	+ **Yields results that allow simple explanation of other features**
* **Derivation of the quantum mechanical hypothesis or χ-hypothesis**
	+ **Three reference states**
		- **To box bottom**
		- **To 1 bar – for calorimetry**
		- **To *P*vap – for isotherm display**
	+ **Perturbation theory**
		- **|*E*a| > |ε|**
		- **|ε| > |*E*a|**
		- **The derivation for |*E*a| > |ε|**
	+ **Stage 1a particle in the box**
		- **Reference state at the bottom of an infinite box**
		- **Difference between an infinite box and a high wide box – big box approximation**
		- **The first molecule creating the first perturbation**
		- **The second molecule affected by the first molecule**
	+ **Stage 1b more adsorbate molecules**
		- **The third molecule**
		- **The Nth molecule**
	+ **Stage 2 the energy with N molecules**
		- **The “controversial” approximation**
	+ **Grand Canonical Partition Function, GCPF**
		- **Take a note – what if the uncovered surface function?**
		- **The final overall GCPF**
		- **The overall equation**
		- **The “layered” equations.**
	+ **Simple interpretation - The classical meanings of χ and Δχ**
		- **χ meaning**
		- **Δχ meaning**
		- **The uses**
* **Fuller’s ASP.**
	+ **Polanyi’s method**
	+ **Examples of ASP publications**
* **Derivation of Excess Surface Work or ESW**
	+ **Derivation from DP**
	+ **ESW formulation – “How to”**
	+ **Energy balance for porosity**
	+ Etc.
* **Cross comparison of χ and ESW**
	+ **Equivalence of *Ē*a = *VH*o?**
* **More about threshold pressure and χς**
	+ **Additional BET disproof**
* **“Layers” in χ**
	+ **The log-law**
	+ **Lemma 1**
	+ **Slightly more than 1 “layer”**
		- **Cannibalization**
		- **Overall equation with half a 2nd layer**
* **Definition of feature instead of “Type”**
* **First feature – the log law**
	+ **AALR example**
	+ **Do, et al., example**
	+ **Example of small amount of 2nd “layer” example**
* **Second feature – heterogeneity**
	+ **Theoretical explanation**
	+ **KJO data showing slight heterogeneity**
	+ **How heterogeneity affects saturation pressure**
	+ **Example of large heterogeneity who?**
	+ **Example of log-law/large external**
* **Third feature – mesoporosity**
	+ **Theoretical explanation for fitting**
	+ **Theoretical explanation for position with χ**
	+ **Examples from**
* **Mixed features –**
	+ **Microporous plus large external area.**
	+ Stop Here – future work:
* **|ε| > |*E*a|**
	+ **H2O and C6H6 on SiO2** may need some new words here. ?-phil and ?-phobe
* **Binary adsorption**

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| The BET model is based on a set of assumptions that include (1) adsorption on a uniform surface, (2) each adsorbed molecule in a layer is a potential adsorption site for the next layer, (3) no steric limitation on the thickness of the multilayer, (4) no interaction between the molecules in the same layer, and (5) the energy of adsorption on the first layer is higher than the rest (Figure 1a). (3) However, as has been pointed out, “[t]he BET model appears to be unrealistic in a number of respects. For example, in addition to the Langmuir concept of an ideal localized monolayer adsorption, it is assumed that all the adsorption sites for multilayer adsorption are energetically identical and that all layers after the first have liquid-like properties.” (2) Furthermore, Rouquerol et al. have even stated that “the BET model does not provide a realistic description of any known physisorption system.” (2) Hence, the previous discussions on the validity and foundation of the BET surface area have centered around the validity of these assumptions, especially for porous and granular systems. (3,11−13)Surface Area Estimation: Replacing the Brunauer–Emmett–Teller Model with the Statistical Thermodynamic Fluctuation Theory Seishi Shimizu\* and Nobuyuki MatubayasiCite this: Langmuir 2022, 38 (26) 7989–8002Publication Date: June 17, 2022https://doi.org/10.1021/acs.langmuir.2c00753Copyright © 2022 The Authors. Published by American Chemical Society |